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㉙ Absorbent for carbon dioxide or for carbon dioxide and oxygen, a method of making the same, and the use of the absorbent in a package.

㉚ Absorbent for carbon dioxide or for carbon dioxide and oxygen, comprising cement brick in the form of shaped bodies, lumps or a powder which, in addition to gel pores, contains larger pores and, for the absorption of oxygen, also iron powder; a method of preparing such absorbent by setting, hardening and drying a cement paste containing cement, a water-soluble inorganic salt, at least 50 parts by weight of water per 100 parts by weight of cement, and for the absorption of oxygen, also iron powder; and the use of said absorbent in a package containing ground or non-ground roasted coffee.

EP 0 142 903 A2

Absorbent for carbon dioxide or for carbon dioxide and oxygen, a method of making the same, and the use of the absorbent in a package.

This invention relates in a first embodiment to an absorbent for carbon dioxide gas and in a second embodiment to an absorbent capable of absorbing both carbon dioxide and oxygen. The invention further relates to methods of preparing such absorbents, and to the use thereof in packages,
5 in particular packages containing roasted coffee.

As is well known, freshly roasted coffee contains a considerable amount of carbon dioxide, which slowly escapes from the coffee. The rate at which this takes place depends on the degree of division of the coffee, and is higher with ground coffee than with unground beans. Furthermore,
10 roasted coffee is highly sensitive to oxygen, which by reacting with coffee components causes rapid aging of the coffee. To prevent such reactions to the extent possible, roasted coffee is often packed in vacuo or under a protective gas, but in neither method of packaging can the packaged coffee be prevented from remaining in contact with a minor quantity of oxygen,
15 because the oxygen cannot be fully excluded. If it is desired for roasted coffee to be packaged in vacuo or under a protective gas, it is necessary to wait until so much CO₂ has escaped from the coffee that the residual concentration is insufficient to remove the vacuum or to cause the package with the protective gas to bulge.

20 For the packaging of roasted coffee, CO₂-permeable foils have been developed. These, however, exhibit the disadvantage that, after some time, oxygen can penetrate the package from the outside. It is also known to provide an excess pressure valve in the package, which permits CO₂ gas collecting in the package to escape when a certain pressure is exceeded. Such valves,
25 however, require complicated and expensive provisions in packaging machines.

The present invention provides an absorbent for carbon dioxide or for carbon dioxide and oxygen, which can be made in a very simple manner

from cheap raw materials, and can easily be packaged along with roasted coffee.

The absorbent according to the invention is characterized, in its first embodiment, by cement brick which, in addition to so-called "gel pores" contains larger pores, and which cement brick has the shape of
5 bodies, lumps, or a powder.

As used herein, and in the appended claims, "cement brick" means the solid product obtained by setting and hardening a cement paste containing cement, water and certain other ingredients.

10 The absorbent according to the invention can be prepared, in its first embodiment, by allowing a cement paste containing cement, a water-soluble salt, and at least 50 parts by weight of water per 100 parts by weight of cement to set and harden, and drying and, if desired, crushing the resulting cement brick.

15 The second embodiment of the absorbent according to the invention is characterized by iron powder containing cement brick which, in addition to so-called "gel pores", contains larger pores, and which cement brick has the shape of bodies, lumps or a powder.

The second embodiment of the absorbent according to the invention
20 can be prepared by allowing a cement paste, containing cement, iron powder, a water-soluble inorganic salt and at least 50 parts by weight of water per 100 parts by weight of cement to set and harden, and drying and, if desired, crushing the resulting cement brick.

As is well known, from a paste containing cement and water, there
25 is formed by setting and hardening cement brick having a Ca(OH)_2 containing porous structure, in which the pore size depends on the water-to-cement weight ratio in the paste. If the water-to-cement ratio is

less than 1:2, small pores are formed only, namely, the so-called "gel pores", but when the water-to-cement ratio is more than a 1:2, larger pores are formed as well.

5 It has been found that the presence of such larger pores is necessary for the present purposes, namely, a rapid absorption of CO_2 and, possibly, oxygen from the ambient atmosphere, in which CO_2 is bonded to the $\text{Ca}(\text{OH})_2$ formed by the reaction of the cement clinker minerals with water, and oxygen is bonded to the iron powder which may be present in the cement brick.

10 The absorbent according to the invention can be made using a commercial cement of current composition. As the CO_2 absorption capacity of the cement brick is dependent upon the $\text{Ca}(\text{OH})_2$ content of the cement brick, cement types which during setting and hardening form relatively much $\text{Ca}(\text{OH})_2$ are preferred. Accordingly, particularly suitable are
15 cement types having a high tricalcium silicate content, such as portland cement, or having a high tricalcium aluminate content, such as aluminum cement (ciment fondu). The CO_2 -absorption capacity can further be increased, as desired, by adding $\text{Ca}(\text{OH})_2$ to the cement paste. The rate of absorption, however, is mainly determined by the presence of
20 large pores in the cement brick, which are formed if the cement paste contains at least 50 parts by weight of water per 100 parts by weight of cement.

When the cement paste contains iron powder, this is incorporated into the porous structure of the cement brick during binding and
25 hardening, where it is available as a potential oxygen binder. As the iron particles are moistened with the $\text{Ca}(\text{OH})_2$ dissolved in moisture residues, which is also present in the porous structure, the pH at the

0142903

iron surface has a value of between 10 and 12. As is well known, in this pH range the iron surface is passivated, i.e., a spontaneous reaction between iron and oxygen (from the air) can hardly, if at all, occur.

If the absorbent is introduced into a CO_2 -rich atmosphere, the pH at the iron surface is reduced until it reaches the level at which the reaction between iron and oxygen is initiated, and oxygen is bonded. In atmospheric air the CO_2 -content is too low to lower the pH of the iron surface sufficiently to make possible that oxygen is bonded. This means that the absorbent according to the invention can be kept in the air without particular precautions.

To produce an absorbent having a favourable porosity, the quantity of water incorporated in the cement paste in preparing the absorbent is preferably 100-200 parts by weight per 100 parts by weight of cement.

In the cement paste, the water-soluble inorganic salt functions as an accelerator of the setting and hardening of the cement. Preferred salts are the chloride, bromide, iodide, chlorate, nitrite, nitrate, or rhodanide of sodium, lithium, ammonium, calcium or magnesium. If no iron powder is incorporated in the cement paste, the salt is preferably used in a proportion of between 1 and 25 parts by weight per 100 parts by weight of cement. When iron powder is incorporated in the cement paste the inorganic salt still has a particular function in the ready absorbent, namely, as an accelerator of oxygen absorption. In that case the salt is preferably used in a proportion of 50-125 parts by weight per 100 parts by weight of cement, in particular of about 100 parts by weight per 100 parts by weight of cement.

The iron powder, if used, does not have to satisfy particular requirements of purity, but without any objection may contain the usual contaminations. Reduced iron powder, electrolytic iron powder and

0142903

atomized iron powder are examples of suitable material. The amount of iron powder in the cement paste can be selected depending on the amount of oxygen to be bonded by the ready absorbent. As the rate of oxygen absorption has been found to depend to a certain extent on the iron content of the absorbent, the proportion of iron powder in the cement paste is preferably at least 50 parts by weight per 100 parts by weight of cement, in particular between 100 and 250 parts by weight per 100 parts by weight of cement. For a good contact between the iron powder in the ready absorbent and the oxygen to be absorbed, it is desirable, that the powder particles should be less than 1 mm, in particular less than 300 μ m.

The starting materials are made up with water to a pasty mixture. If so much water is used that the mixture is too liquid, a thickening agent, for example, on the basis of a carboxy alkyl cellulose, may be added to produce a pasty consistency. Also, fine sand with a particle size of for example 200-300 μ m may be incorporated in the cement paste to promote the formation of the desired porous structure.

The cement paste is homogenized as best as possible and then introduced into suitable moulds, whereafter the paste is allowed to set and harden. The resulting cement bricks are subsequently dried, preferably at 105°C for 1-2 hours, and can then be used as such or be crushed to form lumps or to form a powder.

The resulting absorbent can be successfully used for absorbing carbon dioxide or carbon dioxide and oxygen in a package containing ground or non-ground roasted coffee in a closed envelope. Preferably, the absorbent is introduced into the package in such a manner that it is separated from the coffee by means of a gas-permeable material. If the closed envelope consists of multifold material, the inner or innermost

0142903

wall may be gas-permeable, and the absorbent may be introduced between the inner or innermost wall and the next wall. Owing to the presence of the absorbent according to the invention, in spite of the generation of CO_2 by the roasted coffee, a subatmospheric pressure is generated in the package.

The invention is illustrated in and by the following examples.

EXAMPLE I

Two cement pastes A and B were prepared, having the following compositions:

	<u>A</u>	<u>B</u>
10 portland cement, parts by weight	12	12
water, parts by weight	12	3
CaCl_2 , parts by weight	2	2

The pastes were poured into separate moulds , and left therein at about 50°C for 48 hours. Thereafter the resulting mouldings (20 x 20 x 20 mm) were taken from the moulds and dried at 105°C for 1 hour. Subsequently, tests were conducted, in which the absorption behaviour of absorbent A according to the invention was compared to that of absorbent B, which as a result of the low water-to-cement weight ratio of 1:4 only contained so-called gel pores, and accordingly did not satisfy the present invention. The tests were carried out as follows.

Identical samples of 250 g freshly-roasted ground coffee with a gas content of 0.42 % by weight were introduced into hermetically sealable steel cylinders equipped with a pressure gauge suitable for measuring a subatmospheric pressure. Absorbent A was added to the

0142903

contents of one of the cylinders, and absorbent B to the contents of the second cylinder. After sealing the cylinders, the percentage of CO₂ in the cylinders was measured from time to time, and any subatmospheric pressure was noted. The results are listed in Table A.

5

TABLE A

		<u>test 1 - absorbent A</u>		<u>test 2 - absorbent B</u>	
time (hours)	CO ₂ (vol%)	pressure below atmospheric (cm Hg)	CO ₂ (vol%)	pressure below atmospheric (cm Hg)	
10	0.25	5.7	2	18.5	-
	0.50	5.3	5		
	1.00	4.1	8	16.2	-
	1.25	2.6	12		
	2.00			16.5	-
15	2.50			16.2	4
	2.75			16.0	4
	20.25			1.0	18
	21.00	0.1	17		
	21.25			1.0	19
20	21.75			1.0	19
	22.00	0.1	19		

25 These results show that, in test I, virtually from the beginning, a subatmospheric pressure was generated in the cylinder owing to the rapid absorption of the CO₂ generated by the coffee, which had already partially displaced the air present in the cylinder before it was sealed, by absorbent A according to the invention. On the other hand, in test 2, it took more than 2 hours before any subatmospheric pressure was measured. The rapid absorption of the CO₂ by the absorbent according

0142903

to the invention prevents rupture of a flexible packaging material as a result of excess pressure in the package.

EXAMPLE II

An absorbent C according to the present invention was prepared
5 from a cement paste having the following composition:

10 g portland cement

10 g water

5 g CaCl_2

20 g reduced iron powder (max. particle size 200 μm)

10 First the cement, water and CaCl_2 were mixed to form a viscous
paste, whereafter the iron powder was added with stirring. The paste was
poured into a mould, and left therein at 50°C for 48 hours. The resulting
absorbent C was taken from the mould and dried at 105°C for 1 hour.

Absorbent C was introduced together with 250 g ground coffee,
15 roasted approximately 1 hour before, into a hermetically sealable vessel
just capable of containing the coffee and the absorbent. After sealing
the vessel, the CO_2 and O_2 content in the vessel were measured from
time to time, and a subatmospheric pressure, if any, was noted.

In an analogous manner, a test was conducted with an absorbent D
20 according to the invention, prepared from a cement paste having the
following composition:

8 g portland cement

8 g water

8 g CaCl_2

25 16 g reduced iron powder

Absorbent D was dried at 105°C for 2 hours.

The result of the two tests are listed in Table B.

TABLE B

0142903

test 3 - absorbent C				test 4 - absorbent D			
time (hours)	O ₂ (vol%)	CO ₂ (vol%)	pressure below atmospheric (cm Hg)	time (hours)	O ₂ (vol%)	CO ₂ (vol%)	pressure below atmospheric (cm Hg)
0	17.55	14.7	-	0	15.1	19.04	-
0.6	14.3	19.5	-	0.33	15.1	22.4	-
0.8	15.4	21.9	-	0.66	13.6	21.9	-
1.0	14.3	20.8	-	0.83	12.3	21.3	-
1.4	13.1	19.2	-	1.25	11.2	18.4	-
1.7	12.5	17.0	-	1.5	10.7	17.3	1
1.9	12.0	15.2	1	1.75	9.5	16.3	3
2.15	11.6	13.3	3	2.17	8.5	15.0	8
2.65	10.3	12.0	8	2.58	8.0	14.1	10
19.6	0.9	0.36	26	18.92	1.7	2.1	25
20.2	0.71	0.32	26	20.08	1.6	1.7	25
22.1	0.67	0.28	29	20.73	1.4	1.6	26
25.2	0.65	0.24	29	25.0	1.2	1.5	27
92.5	0.62	0.05	29	92.1	0.6	0.10	30
116.5	0.60	0.05	28	116.0	0.6	0.07	30
140.5	0.57	0.01	29	164.0	0.6	-	32
164.5	0.55	0.01	29				

These results show that the absorbent according to the second
embodiment of the invention is effectively capable of simultaneously
absorbing oxygen and CO₂.

EXAMPLE III

In order to show that the absorbent according to the second
embodiment of the invention does not lose its capacity of absorbing
oxygen from contact with oxygen in the air, the absorbent D used in

0142903

test 4 (Example II) after the test was kept in the air for two months.
The absorbent was dried at 105°C for 1 hour, and subsequently tested,
in the manner described in Example II, with freshly-roasted ground coffee
with a gas content of 0.45 percent by weight. The results are listed in
5 Table C.

TABLE C

	time (hours)	O ₂ (vol %)	CO ₂ (vol %)
	4	10.8	8.3
	6	8.0	5.4
10	70	0.7	0.1

EXAMPLE IV

In the manner described in Example II, an absorbent was prepared
from a cement paste having the following composition:

- 10 g portland cement
- 15 10 g water
- 2 g CaCl₂
- 10 g reduced iron powder

and subsequently tested in the manner described.

The results are listed in Table D.

TABLE D

	time (hours)	O ₂ (vol %)	CO ₂ (vol %)
	0	18.6	2.3
	0.25	18.3	2.4
25	0.50	18.3	2.7
	1.25	18.0	2.5
	3.25	17.9	1.4

0142903

TABLE D (continued)

<u>time</u> <u>(hours)</u>	<u>O₂</u> <u>(vol %)</u>	<u>CO₂</u> <u>(vol %)</u>
4.25	17.4	1.1
21.0	16.8	< 0.1
26.0	16.2	< 0.1

These results show that the absorbent effectively absorbed the CO₂ but, as a result of the too low salt content, was insufficiently capable of absorbing oxygen.

C L A I M S

1. Absorbent for carbon dioxide, characterized by cement brick which, in addition to so-called "gel pores" contains larger pores, which cement brick has the form of bodies, lumps or a powder.
2. Absorbent for carbon dioxide and oxygen, characterized by iron
5 powder containing cement brick which, in addition to "gel pores" contains larger pores, which cement brick has the form of bodies, lumps, or a powder.
3. A method of preparing an absorbent according to claim 1, characterized by allowing a cement paste containing cement, a water-soluble
10 inorganic salt and at least 50 parts by weight of water per 100 parts by weight of cement to set and harden, and drying and, if desired, crushing the resulting cement brick.
4. A method of preparing an absorbent according to claim 2,
15 characterized by allowing a cement paste containing cement, iron powder, a water-soluble inorganic salt and at least 50 parts by weight of water per 100 parts by weight of cement to set and harden, and drying and, if desired, crushing, the resulting cement brick.
5. A method according to claim 3 or 4, characterized by using as the cement portland cement or aluminum cement.
- 20 6. A method according to claims 3 - 5, characterized in that the cement paste contains 100-200 parts by weight of water per 100 parts by weight of cement.
7. A method according to claims 3 - 6, characterized by using as the inorganic salt a chloride, bromide, iodide, chlorate, nitrite, nitrate,
25 or rhodanide of sodium, potassium, lithium, ammonium, calcium, or magnesium.

0142903

8. A method according to claim 3, characterized in that the cement paste contains 1-25 parts by weight of inorganic salt per 100 parts by weight of cement.
9. A method according to claim 4, characterized in that the cement paste contains 50-125 parts by weight of inorganic salt per 100 parts by weight of cement.
10. A method according to claim 4, characterized by using iron powder having an average particle size of less than 300 μ m.
11. A method according to claim 4 or 10, characterized in that the cement paste contains at least 50 parts by weight of iron powder per 100 parts by weight of cement.
12. A method according to claim 11, characterized in that the cement paste contains 100-250 parts by weight of iron powder per 100 parts by weight of cement.
13. A method according to claims 3-12, characterized by additionally incorporating calcium hydroxide in the cement paste.
14. A package containing ground or non-ground roasted coffee in a sealed gas-tight envelope, characterized in that the envelope contains an absorbent according to claim 1 or 2, or produced by the method according to any of claims 3 - 13.
15. A package according to claim 14, characterized in that the absorbent is separated from the coffee by means of a gas-permeable material.